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McCready

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[54] **THERMOPLASTIC POLYETHERIMIDE
ESTER ELASTOMERS**

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528/292; 528/295.3; 528/296**

[58] Field of Search **528/289, 292, 296, 295.3;
525/444.5**

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[57] **ABSTRACT**

Novel polyetherimide esters are prepared from diols, dicarboxylic acids and polyoxyalkylene diimide diacids. These compositions have many excellent properties which make them particularly useful for extrusion and molding applications.

27 Claims, No Drawings

THERMOPLASTIC POLYETHERIMIDE ESTER ELASTOMERS

The present invention relates to novel thermoplastic elastomers having excellent stress-strain properties, low tensile set, high melting temperatures and/or excellent strength/toughness characteristics as well as superior flexibility which are especially suitable for molding and extrusion applications. Specifically, novel polyetherimide esters having the above-mentioned properties have been prepared from one or more diols, one or more dicarboxylic acids and, most importantly, one or more high molecular weight polyoxyalkylene diimide diacids.

Polyether ester imides are well known having been described in numerous publications and patents including for example, Honore et al, "Synthesis and Study of Various Reactive Oligomers and of Poly(ester-imide-ether)s", *European Polymer Journal* Vol. 16, pp. 909-916, Oct. 12, 1979; and in Kluber et al, U.S. Pat. No. 3,274,159 and Wolfe Jr., U.S. Pat. Nos. 4,371,692 and 4,371,693, respectively. However, none of the prior art references teach or suggest the novel poly(etherimide ester) compositions of the present invention. Furthermore, none of these references provide polyetherimide ester resins having the excellent physical properties, including high melting point and excellent flexibility, as mentioned above, combined with the rapid crystallization rate and excellent moldability characteristics of the novel polyetherimide esters of the present invention.

Specifically, applicants have now found a novel class of poly(etherimide ester) elastomers which are particularly suited for molding and/or extrusion applications and which are characterized as having one or more of the following enhanced properties: stress-strain resistance, toughness/strength, and tensile set at low flexural modulus combined with rapid crystallization rates and excellent moldability as demonstrated by short cycle times and good mold releasability, respectively.

The novel poly(etherimide esters) of the present invention may be either random or block and are prepared by conventional processes from (a) one or more diols, (b) one or more dicarboxylic acids and (c) one or more polyoxyalkylene diimide diacids. Preferred compositions encompassed by the present invention may be prepared from (a) one or more C₂-C₁₅ aliphatic and/or cycloaliphatic diols, (b) one or more C₄-C₁₆ aliphatic, cycloaliphatic and/or aromatic dicarboxylic acids or ester derivatives thereof and (c) one or more polyoxyalkylene diimide diacid employed is generally dependent upon the desired properties of the resultant polyetherimide ester. In general, the weight ratio of polyoxyalkylene diimide diacid (c) to dicarboxylic acid (b) is from about 0.25 to 2.0, preferably from about 0.4 to about 1.4. Finally, the compositions may contain and preferably do contain additional stabilizers for even greater stabilization and low temperature impact strength.

Suitable diols (a) for use in preparing the compositions of the present invention include saturated and unsaturated aliphatic and cycloaliphatic dihydroxy compounds as well as aromatic dihydroxy compounds. These diols are preferably of a low molecular weight, i.e. having a molecular weight of about 250 or less. When used herein, the term "diols" and "low molecular weight diols" should be construed to include equivalent

ester forming derivatives thereof, provided, however, that the molecular weight requirement pertains to the diol only and not to its derivatives. Exemplary of ester forming derivatives there may be given the acetates of the diols as well as for example ethylene oxide or ethylene carbonate for ethylene glycol.

Preferred saturated and unsaturated aliphatic and cycloaliphatic diols are those having from about 2 to 15 carbon atoms. Exemplary of these diols there may be given ethyleneglycol, propanediol, butanediol, pentanediol, 2-methyl propanediol, 2,2-dimethyl propanediol, hexanediol, decanediol, 1,2-, 1,3- and 1,4-dihydroxy cyclohexane; 1,2-, 1,3- and 1,4-cyclohexane dimethanol; butene diol; hexene diol, etc. Especially preferred are 1,4-butanediol and mixtures thereof with hexanediol or butenediol, most preferably 1,4-butanediol.

Aromatic diols suitable for use in the practice of the present invention are generally those having from 6 to about 15 carbon atoms. Included among the aromatic dihydroxy compounds are resorcinol; hydroquinone; 1,5-dihydroxy naphthalene; 4,4'-dihydroxy diphenyl; bis(p-hydroxy phenyl)methane and bis(p-hydroxy phenyl) 2,2-propane.

Especially preferred diols are the saturated aliphatic diols, mixtures thereof and mixtures of a saturated diol(s) with an unsaturated diol(s), wherein each diol contains from 2 to about 8 carbon atoms. Where more than one diol is employed, it is preferred that at least about 60 mole %, based on the total diol content, be the same diol, most preferably at least 80 mole %. As mentioned above, the preferred compositions are those in which 1,4-butanediol is present in a predominant amount, most preferably when 1,4-butanediol is the only diol.

Dicarboxylic acids (b) which are suitable for use in the practice of the present invention are aliphatic, cycloaliphatic, and/or aromatic dicarboxylic acids. These acids are preferably of a low molecular weight, i.e., having a molecular weight of less than about 300; however, higher molecular weight dicarboxylic acids, especially dimer acids, may also be used. The term "dicarboxylic acids" as used herein, includes equivalents of dicarboxylic acids having two functional carboxyl groups which perform substantially like dicarboxylic acids in reaction with glycols and diols in forming polyester polymers. These equivalents include esters and ester-forming derivatives, such as acid halides and anhydrides. The molecular weight preference, mentioned above, pertains to the acid and not to its equivalent ester or ester-forming derivative. Thus, an ester of a dicarboxylic acid having a molecular weight greater than 300 or an acid equivalent of a dicarboxylic acid having a molecular weight greater than 300 are included provided the acid has a molecular weight below about 300. Additionally, the dicarboxylic acids may contain any substituent group(s) or combinations which do not substantially interfere with the polymer formation and use of the polymer of this invention.

Aliphatic dicarboxylic acids, as the term is used herein, refers to carboxylic acids having two carboxyl groups each of which is attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and is in a ring, the acid is cycloaliphatic.

Aromatic dicarboxylic acids, as the term is used herein, are dicarboxylic acids having two carboxyl groups each of which is attached to a carbon atom in an isolated or fused benzene ring system. It is not necessary

that both functional carboxyl groups be attached to the same aromatic ring and where more than one ring is present, they can be joined by aliphatic or aromatic divalent radicals or divalent radicals such as —O— or —SO₂—.

Representative aliphatic and cycloaliphatic acids which can be used for this invention are sebacic acid, 1,2-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, adipic acid, glutaric acid, succinic acid, oxalic acid, azelaic acid, diethylmalonic acid, allylmalonic acid, dimer acid, 4-cyclohexene-1,2-dicarboxylic acid, 2-ethylsuberic acid, tetramethylsuccinic acid, cyclopentanedicarboxylic acid, decahydro-1,5-naphthalene dicarboxylic acid, 4,4'-bicyclohexyl dicarboxylic acid, decahydro-2,6-naphthalene dicarboxylic acid, 4,4 methylenebis(cyclohexane carboxylic acid), 3,4-furan dicarboxylic acid, and 1,1-cyclobutane dicarboxylic acid. Preferred aliphatic acids are cyclohexane dicarboxylic acids, sebacic acid, dimer acid, glutaric acid, azelaic acid and adipic acid.

Representative aromatic dicarboxylic acids which can be used include terephthalic, phthalic and isophthalic acids, bi-benzoic acid, substituted dicarboxy compounds with two benzene nuclei such as bis(p-carboxyphenyl) methane, oxybis(benzoic acid), ethylene-1,2-bis-(p-oxybenzoic acid), 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, phenanthrene dicarboxylic acid, anthracene dicarboxylic acid, 4,4'-sulfonyl dibenzoic acid, and halo and C₁-C₁₂ alkyl, alkoxy, and aryl ring substitution derivatives thereof. Hydroxy acids such as p(β-hydroxyethoxy)benzoic acid can also be used provided an aromatic dicarboxylic acid is also present.

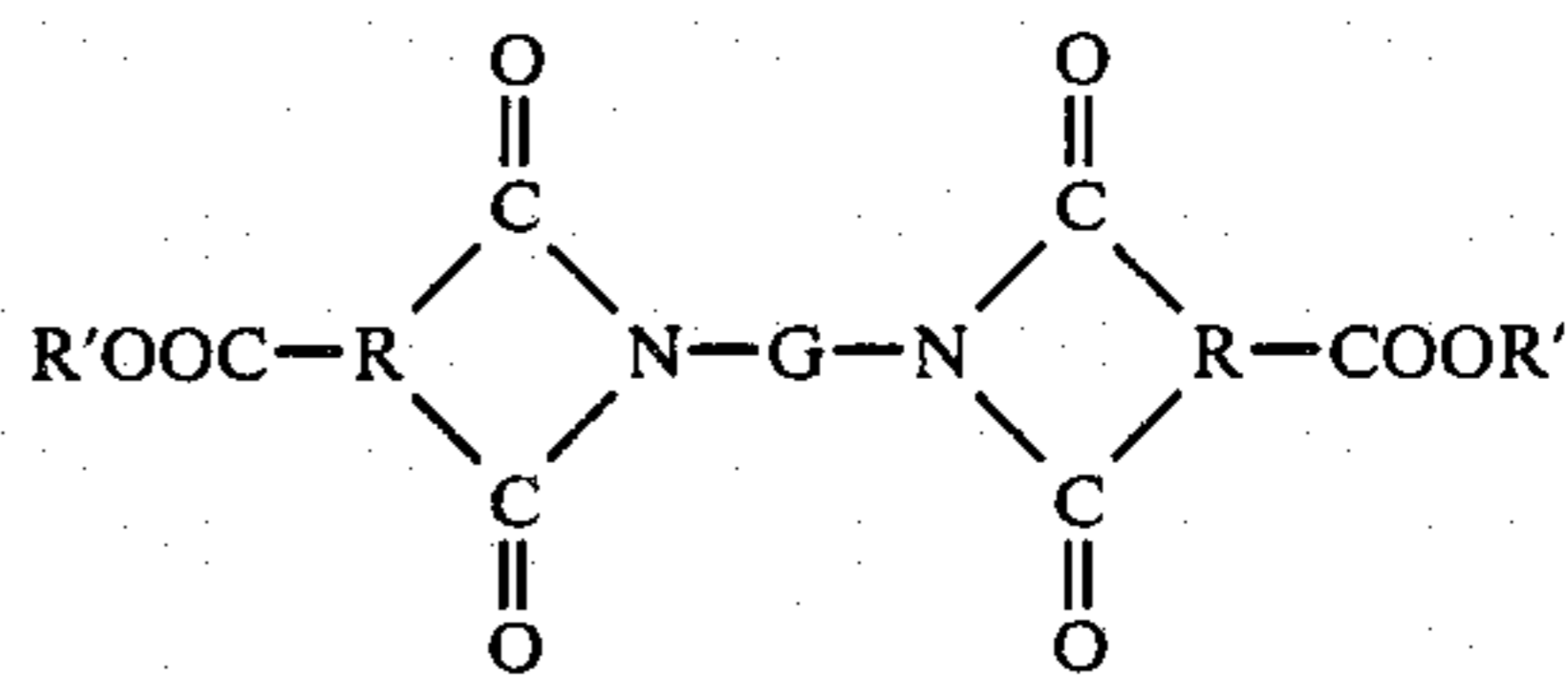
Preferred dicarboxylic acids for the preparation of the polyetherimide esters of the present invention are the aromatic dicarboxylic acids, mixtures thereof and mixtures of one or more dicarboxylic acid with an aliphatic and/or cycloaliphatic dicarboxylic acid, most preferably the aromatic dicarboxylic acids. Among the aromatic acids, those with 8-16 carbon atoms are preferred, particularly the benzene dicarboxylic acids, i.e., phthalic, terephthalic and isophthalic acids and their dimethyl derivatives. Especially preferred is dimethyl terephthalate.

Finally, where mixtures of dicarboxylic acids are employed in the practice of the present invention, it is preferred that at least about 60 mole %, preferably at least about 80 mole %, based on 100 mole % of dicarboxylic acid (b) be of the same dicarboxylic acid or ester derivative thereof. As mentioned above, the preferred compositions are those in which dimethylterephthalate is the predominant dicarboxylic acid, most preferably when dimethylterephthalate is the only dicarboxylic acid.

Polyoxyalkylene diimide diacids (c) suitable for use herein are high molecular weight diimide diacids wherein the average molecular weight is greater than about 700, most preferably greater than about 900. They may be prepared by the imidization reaction of one or more tricarboxylic acid compounds containing two vicinal carboxyl groups or an anhydride group and an additional carboxyl group which must be esterifiable and preferably is nonimidizable with a high molecular weight polyoxyalkylene diamine. These polyoxyalkylene diimide diacids and processes for their preparation are more fully disclosed in applicant's copending, U.S.

patent application Ser. No. 665,192, filed Oct. 26, 1984 entitled "High Molecular Weight Diimide Diacids and Diimide Diesters of Tricarboxylic Anhydrides", incorporated herein by reference.

In general, the polyoxyalkylene diimide diacids useful herein may be characterized by the following formula:



wherein each R is independently a trivalent organic radical, preferably a C₂ to C₂₀ aliphatic, aromatic or cycloaliphatic trivalent organic radical; each R' is independently hydrogen or a monovalent organic radical preferably selected from the group consisting of C₁ to C₆ aliphatic and cycloaliphatic radicals and C₆ to C₁₂ aromatic radicals, e.g. benzyl, most preferably hydrogen; and G is the radical remaining after the removal of the terminal (or as nearly terminal as possible) hydroxy groups of a long chain ether glycol having an average molecular weight of from about 600 to about 12000, preferably from about 900 to about 4000, and a carbon-to-oxygen ratio of from about 1.8 to about 4.3.

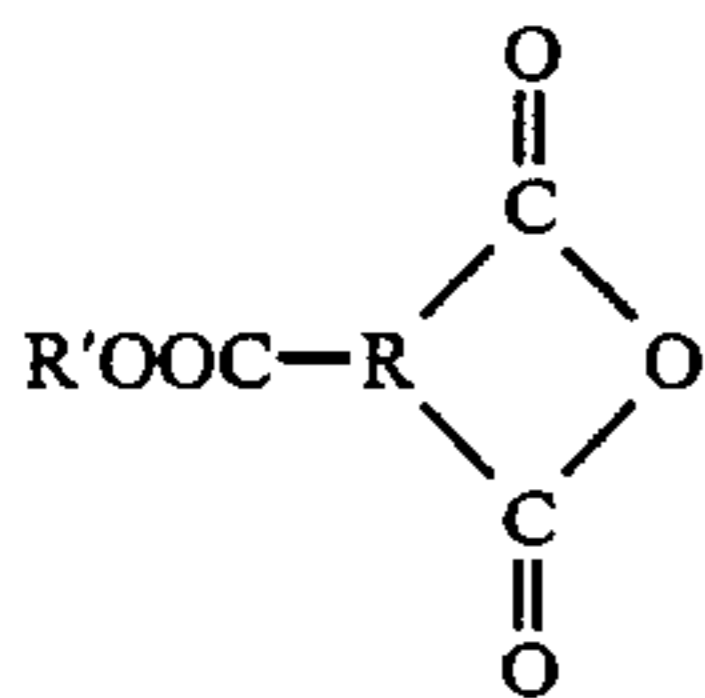
Representative long chain ether glycols from which the polyoxyalkylene diamine is prepared include poly(ethylene ether)glycol; poly(propylene ether)glycol; poly(tetramethylene ether)glycol; random or block copolymers of ethylene oxide and propylene oxide, including propylene oxide terminated poly(ethylene ether)glycol; and random or block copolymers of tetrahydrofuran with minor amounts of a second monomer such as methyl tetrahydrofuran (used in proportion such that the carbon-to-oxygen mole ratio in the glycol does not exceed about 4.3). Especially preferred poly(alkylene ether)glycols are poly(propylene ether) glycol and poly(ethylene ether)glycols end capped with poly(propylene ether)glycol and/or propylene oxide.

In general, the polyoxyalkylene diamines useful within the scope of the present invention will have an average molecular weight of from about 600 to 12000, preferably from about 900 to about 4000.

The tricarboxylic component may be almost any carboxylic acid anhydride containing an additional carboxylic group or the corresponding acid thereof containing two imide-forming vicinal carboxyl groups in lieu of the anhydride group. Mixtures thereof are also suitable. The additional carboxylic group must be esterifiable and preferably is substantially nonimidizable.

Further, while trimellitic anhydride is preferred as the tricarboxylic component, any of a number of suitable tricarboxylic acid constituents will occur to those skilled in the art including 2,6,7 naphthalene tricarboxylic anhydride; 3,3',4 diphenyl tricarboxylic anhydride; 3,3',4 benzophenone tricarboxylic anhydride; 1,3,4 cyclopentane tricarboxylic anhydride; 2,2',3 diphenyl tricarboxylic anhydride; diphenyl sulfone - 3,3',4 tricarboxylic anhydride, ethylene tricarboxylic anhydride; 1,2,5 naphthalene tricarboxylic anhydride; 1,2,4 butane tricarboxylic anhydride; diphenyl isopropylidene 3,3',4 tricarboxylic anhydride; 3,4 dicarboxyphenyl 3'-carboxylphenyl ether anhydride; 1,3,4 cyclohexane tricarbox-

ylic anhydride; etc. These tricarboxylic acid materials can be characterized by the following formula:



where R is a trivalent organic radical, preferably a C₂ to C₂₀ aliphatic, aromatic, or cycloaliphatic trivalent organic radical and R' is preferably hydrogen or a monovalent organic radical preferably selected from the group consisting of C₁ to C₆ aliphatic and/or cycloaliphatic radicals and C₆ to C₁₂ aromatic radicals, e.g. benzy; most preferably hydrogen.

Briefly, these polyoxyalkylene diimide diacids may be prepared by known imidization reactions including melt synthesis or by synthesizing in a solvent system. Such reactions will generally occur at temperatures of from 100° C. to 300° C., preferably at from about 150° C. to about 250° C. while drawing off water or in a solvent system at the reflux temperature of the solvent or azeotropic (solvent) mixture.

Although the weight ratio of the above ingredients is not critical, it is preferred that the diol be present in at least a molar equivalent amount, preferably a molar excess, most preferably at least 150 mole % based on the moles of dicarboxylic acid (b) and polyoxyalkylene diimide diacid (c) combined. Such molar excess of diol will allow for optimal yields, based on the amount of acids, while accounting for the loss of diol during esterification/condensation.

Further, while the weight ratio of dicarboxylic acid (b) to polyoxyalkylene diimide diacid (c) is not critical to form the novel polyetherimide esters of the present invention, preferred compositions are those in which the weight ratio of the polyoxyalkylene diimide diacid (c) to dicarboxylic acid (b) is from about 0.25 to about 2, preferably from about 0.4 to about 1.4. The actual weight ratio employed will be dependent upon the specific polyoxyalkylene diimide diacid used and more importantly, the desired physical and chemical properties of the resultant polyetherimide ester. In general, the lower the ratio of polyoxyalkylene diimide diester to dicarboxylic acid the better the strength, crystallization and heat distortion properties of the polymer. Alternatively, the higher the ratio, the better the flexibility, tensile set and low temperature impact characteristics.

In its preferred embodiments, the compositions of the present invention will comprise the reaction product of dimethylterephthalate, optimally with up to 40 mole % of another dicarboxylic acid; 1,4-butanediol, optionally with up to 40 mole % of another saturated or unsaturated aliphatic and/or cycloaliphatic diol; and a polyoxyalkylene diimide diacid prepared from a polyoxyalkylene dimine of molecular weight of from about 600 to about 12000, preferably from about 900 to about 4000, and trimellitic anhydride. In its most preferred embodiments, the diol will be 100 mole % 1,4-butanediol and the dicarboxylic acid 100 mole % dimethylterephthalate.

The novel polyetherimide esters described herein may be prepared by conventional esterification/condensation reactions for the production of polyesters. Exemplary of the processes that may be practiced are as set forth in, for example, U.S. Pat. Nos. 3,023,192;

3,763,109; 3,651,014; 3,663,653 and 3,801,547, herein incorporated by reference. Additionally, these compositions may be prepared by such processes and other known processes to effect random copolymers, block copolymers or hybrids thereof wherein both random and block units are present.

It is customary and preferred to utilize a catalyst in the process for the production of the polyetherimide esters of the present invention. In general, any of the known ester-interchange and polycondensation catalysts may be used. Although two separate catalysts or catalyst systems may be used, one for ester interchange and one for polycondensation, it is preferred, where appropriate, to use one catalyst or catalyst system for both. In those instances where two separate catalysts are used, it is preferred and advantageous to render the ester-interchange catalyst ineffective following the completion of the precondensation reaction by means of known catalyst inhibitors or quenchers, in particular, phosphorus compounds such as phosphoric acid, phosphonic acid, phosphonic acid and the alkyl or aryl esters or salts thereof, in order to increase the thermal stability of the resultant polymer.

Exemplary of the suitable known catalysts there may be given the acetates, carboxylates, hydroxides, oxides, alcoholates or organic complex compounds of zinc, manganese, antimony, cobalt, lead, calcium and the alkali metals insofar as these compounds are soluble in the reaction mixture. Specific examples include, zinc acetate, calcium acetate and combinations thereof with antimony tri-oxide and the like. These catalysts as well as additional useful catalysts are described in U.S. Pat. Nos. 2,465,319; 2,534,028; 2,850,483; 2,892,815; 2,937,160; 2,998,412; 3,047,539; 3,110,693 and 3,385,830, among others, incorporated herein by reference.

Where the reactants and reactions allow, it is preferred to use the titanium catalysts including the inorganic and organic titanium containing catalysts, such as those described in, for example, Nos. 2,720,502; 2,727,881; 2,729,619; 2,822,348; 2,906,737; 3,047,515; 3,056,817; 3,056,818; and 3,075,952 among others, incorporated herein by reference. Especially preferred are the organic titanates such as tetra-butyl titanate, tetraisopropyl titanate and tetra-octyl titanate and the complex titanates derived from alkali or alkaline earth metal alkoxides and titanate esters, most preferably the organic titanates. These too may be used alone or in combination with other catalysts such as for example, zinc acetate, manganese acetate or antimony trioxide, and/or with a catalyst quencher as described above.

Although the novel polyetherimide ester of the present invention possess many desirable properties, it is preferred to stabilize certain of the compositions to heat, oxidation, radiation by UV light and the like. This can be accomplished by incorporating stabilizer materials into the compositions either during production or while in a hot melt stage following polymerization. The particular stabilizers useful herein are any of those known in the art which are suitable for polyetherimide esters.

Satisfactory stabilizers comprise phenols and their derivatives, amines and their derivatives, compounds containing both hydroxyl and amine groups, hydroxyazines, oximes, polymeric phenolic esters and salts of multivalent metals in which the metal is in its lower valence state.

Representative phenol derivatives useful as stabilizers include 3,5-di-tert-butyl-4-hydroxy hydrocinnamic triester with 1,3,5-tris-(2-hydroxyethyl)-s-triazine-2,4,6-(1H,3H,5H)trione; 4,4'-bis(2,6-ditertiary-butylphenol); 1,3,5-trimethyl-2,4,6-tris(3,5-ditertiary-butyl-4-hydroxybenzyl)benzene and 4,4'-butylidene-bis(6-tertiary-butyl-m-cresol). Various inorganic metal salts or hydroxides can be used as well as organic complexes such as nickel dibutyl dithiocarbonate, manganous salicylate and copper 3-phenyl-salicylate. Typical amine stabilizers include N,N'-bis(betanaphthyl)-p-phenylene diamine; N,N'-bis(1-methylheptyl)-p-phenylene diamine and either phenyl-betanaphthyl amine or its reaction products with aldehydes. Mixtures of hindered phenols with esters of thiodipropionic acid, mercaptides and phosphite esters are particularly useful. Additional stabilization to ultraviolet light can be obtained by compounding with various UV absorbers such as substituted benzophenones and/or benzotriazoles.

Optionally, it may be desirable to add a minor amount, up to about 20 mole %, preferably up to about 10 mole %, based on the moles of the polyoxyalkylene diimide diacid, of a tricarboxylic component to the reaction mixture. While higher amounts of the tricarboxylic component may be used, this has the disadvantage of reducing some of the beneficial properties of the present polymers. Suitable tricarboxylic components are the same as identified above for the preparation of the polyoxyalkylene diimide diacid. While it is preferred that the additional tricarboxylic component be the same as used in the preparation of the polyoxyalkylene diimide diacid, it is not necessary. The addition of the tricarboxylic acid component will have the added benefit of picking up and reacting with any residual, unreacted amine groups and, consequently, aiding in the viscosity build of the polymer itself.

Further, the properties of these polyesters can be modified by incorporation of various conventional inorganic fillers such as carbon black, silica gel, alumina, clays and chopped fiberglass. These may be incorporated in amounts up to 50% by weight, preferably up to about 30% by weight. In general, these additives have the effect of increasing the modulus of the material at various elongations.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are presented as illustrative of the present invention and are not to be construed as limiting thereof.

Physical properties were determined according the proper ASTM methods as follows:

Flexural Modulus	ASTM D 790
Tensile Strength	ASTM D 638
Tensile Elongation	ASTM D 638
Shore D Hardness	ASTM D 2240
Tensile Set	ASTM D 412

In general, all compositions were prepared by placing all reactants in the reaction vessel and heating to 180° C. After the theoretical amount of methanol was removed, the pot temperature was increased to about 250° C. and a vacuum applied (<1 mm Hg) until the desired viscosity polymer was obtained. All reactions, unless otherwise specified were catalyzed with tetraoctyl titanate catalyst.

Diimide Diacid A

A polyoxyalkylene diimide diacid was prepared by the imidization of trimellitic anhydride with Texaco Chemical Company's Jeffamine® D2000, a polypropylene ether diamine, average molecular weight 2000.

Diimide Diacid B

A second polyoxyalkylene diimide diacid was prepared by the imidization of trimellitic anhydride with Texaco Chemical Company's Jeffamine ED-900, a predominately polyethylene oxide backbone, copoly(ethylene oxide-propylene oxide) diamine, average molecular weight 900.

Diimide Diacid C

A third polyoxyalkylene diimide diacid was prepared by the imidization of trimellitic anhydride with Texaco Chemical Company's Jeffamine ED-2001, a predominately polyethylene oxide backbone, copoly(ethylene oxide-propylene oxide)diamine, average molecular weight 2000.

EXAMPLES 1-9

Two series of compositions were prepared, one with Diimide Diacid A and the other with Diimide Diacid B at various weight ratios to dicarboxylic acid. The compositions were as presented in Table 1. All reactants are in parts by weight. Additionally, each composition contained about 3% by weight based on the diimide diacid of a thermal stabilizer.

The elastomeric polymers of these examples had excellent physical properties and had surprisingly superior processability and moldability characteristics.

TABLE 1

	1	2	3	4	5	6	7	8	9
COMPOSITION									
1,4-Butanediol	36	33	32	30	27	36	33	32	30
Dimethyl terephthalate	46	42	40	38	34	46	42	40	38
Diimide Diacid A	18	25	28	32	39	—	—	—	—
Diimide Diacid B	—	—	—	—	—	18	25	28	32
Wt. Ratio of Diimide Diacid/DMT	.4	.6	.7	.85	1.15	.4	.6	.7	.85
Trimellitic Anhydride	7.1	7.3	7.2	7.4	6.8	3.2	3.3	3.2	3.3
mole % based on Diimide Diacid									
PROPERTIES									
Melting Point, °C.	215	214	210	203	201	208	196	194	190
Flexural Modulus, psi × 10 ³	63	32	24	16	14.5	52	33	25	20
Tensile Set, %	36	28	25	19	—	31	30	21	20

EXAMPLES 10-22

Several additional compositions within the scope of the present invention were prepared demonstrating various different embodiments hereof. For example, Example 10 demonstrates a composition derived from a mixture of dimethylterephthalate and isophthalic acid and Examples 11, 15, 17 and 21 demonstrates the use of dimer acid (Hystrene® 3695—Witco Chemical Corporation).

Finally, Example 16 demonstrate the use of ethylene glycol as the diol component (this reaction used antimony oxide and zinc acetates as catalysts with a phosphite catalyst quencher). Only those examples as indicated contained a thermal stabilizer. The composition and physical properties of these examples were as set forth in Table 2. All amounts are in parts by weight unless otherwise specified. A comparison of Example 6, above, with Example 12 demonstrates the improved properties obtained by use of stabilizer and excess trimellitic anhydride.

TABLE 2

	10	11	12	13	14	15	16	17	18	19	20	21	22
COMPOSITION													
1,4-Butanediol	21	30	36	30	30	32	—	31	27	21	35	32	30
Ethylene glycol	—	—	—	—	—	—	22	—	—	—	—	—	—
Dimethyl terephthalate	28	36	46	40	40	38	35	37	32	35	46	38	38
Isophthalic Acid	7	—	—	—	—	—	—	—	—	—	—	—	—
Dimer Acid	—	7	—	—	—	10.5	—	5	—	—	—	5	—
Diimide Diacid A	44	—	—	—	—	—	44	27	41	44	19	25	32
Diimide Diacid B	—	27	18	—	—	20	—	—	—	—	—	—	—
Diimide Diacid C	—	—	—	30	30	—	—	—	—	—	—	—	—
Thermal Stabilizer ^a	5	—	—	—	—	—	5	—	4.3	5	5	5	5
Wt. Ratio of Diimide Diacid/Dicarboxylic Acid (excluding Dimer Acid)	1.27	.74	.4	.77	.77	.52	1.27	.75	1.30	1.25	.41	.65	.82
PROPERTIES													
Melting Point, °C.	162	191	210	206	211	193	226	201	197	193	219	201	211
Flexural Modulus, psi × 10 ³	4.9	19.2	45.2	24.6	22	—	4.5	16.9	7.0	—	49	18	22
Tensile Strength, psi × 10 ³	5.0	2.4	4.5	2.8	2.9	—	3.5	2.4	6.7	—	—	—	—
Tensile Elongation %	1143	619	554	786	614	—	143	334	881	—	—	—	—
Shore D Hardness	31	48	61	47	49	—	30	48	37	—	—	—	—
Tensile Set, %	—	—	—	25	—	—	—	—	—	—	—	—	—

^ain wt. % based on amount of diimide diacid.

EXAMPLES 23-27

Additional compositions were prepared again further demonstrating the broad scope of the present invention wherein both stabilizer and additional trimellitic anhydride were added to the reaction mix. The compositions and the physical properties thereof were as shown in Example 3.

TABLE 3

	23	24	25	26	27
COMPOSITION					
1,4-Butanediol	33	23	23	15	14
1,6-Hexanediol	—	7.5	—	10	9
Dimethyl terephthalate	39	46.5	—	33	36
Isophthalic Acid	—	—	36	7	—
Azelaic Acid	9	—	—	—	—
Diimide Diacid A	19	23	41	36	41
Thermal stabilizer ^a	3.7	3	5.5	7	5.5
Trimellitic Anhydride ^b	8.7	7.4	5	9	7.3
PROPERTIES					

TABLE 3-continued

	23	24	25	26	27
Melting Point	184	178	114	ND	ND

^aSee Table 2, note ^a

^bin mole % based on number of moles of Diimide Diacid

Obviously, other modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope as defined by the appended claims.

I claim:

1. A polyetherimide ester composition comprising the reaction product of

- one or more low molecular weight diols,
- one or more dicarboxylic acids, and
- one or more polyoxyalkylene diimide diacids.

2. The composition of claim 1 wherein the diol component (a) is a C₂ to C₁₅ aliphatic or cycloaliphatic diol or a mixture thereof.

3. The composition of claim 2 wherein the diol component (a) is from about 60 to 100 mole % 1,4-butanediol.

4. The composition of claim 2 wherein the diol component (a) is from about 80 to 100 mole % 1,4-butanediol.

5. The composition of claim 2 wherein the diol is 1,4-butanediol.

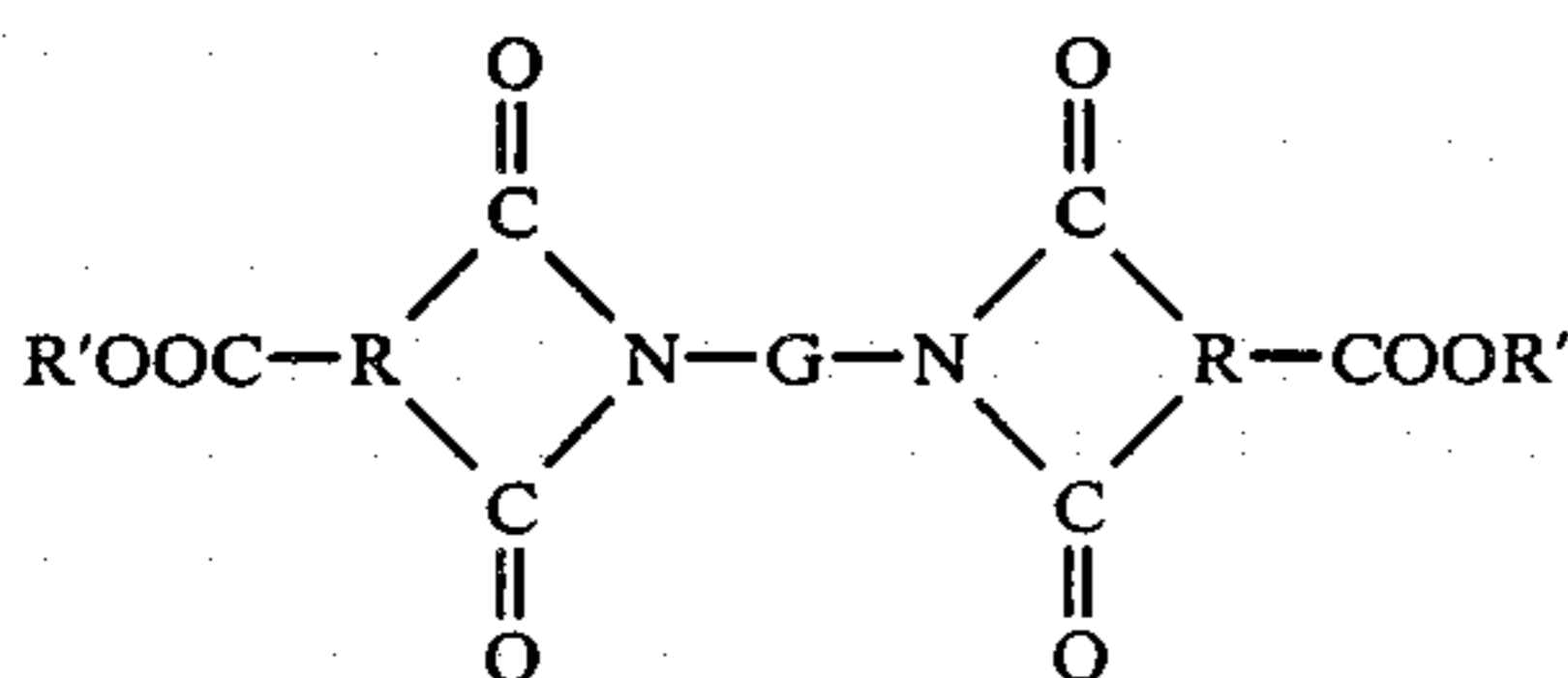
6. The composition of claim 1 wherein the dicarboxylic acid component (b) is selected from the group consisting of C₂ to C₁₆ aliphatic and/or cycloaliphatic dicarboxylic acid or a C₆ to C₁₆ aromatic dicarboxylic acid or the ester equivalents thereof and mixtures thereof.

7. The composition of claim 6 wherein the dicarboxylic acid component (b) is from about 60 to 100 mole % dimethyl terephthalate.

8. The composition of claim 6 wherein the dicarboxylic acid component (b) is from about 80 to 100 mole % dimethyl terephthalate.

9. The composition of claim 6 wherein the dicarboxylic acid component (b) is dimethyl terephthalate.

10. The composition of claim 1 wherein the polyoxyalkylene diimide diacid component (c) is derived from one or more polyoxyalkylene diamines and one or more tricarboxylic acid compounds containing two vicinal carboxyl groups or an anhydride group and an additional carboxyl group, and is characterized by the following formula:



wherein each R is independently selected from the group consisting of C₂ to C₂₀ aliphatic and cycloaliphatic trivalent organic radicals and C₆ to C₂₀ aromatic trivalent organic radicals; each R' is independently selected from the group consisting of hydrogen, C₁ to C₆ aliphatic and cycloaliphatic monovalent organic radicals and C₆ to C₁₂ aromatic monovalent organic radicals, and G is the radical remaining after removal of the hydroxy groups of a long chain ether glycol having an average molecular weight of from about 600 to 12000.

11. The composition of claim 10 wherein the polyoxyalkylene diimide diacid is such that each R is a C₆ trivalent aromatic hydrocarbon radical, each R' is hydrogen and G is the radical remaining after removal of the hydroxy groups of a long chain ether glycol having an average molecular weight of from about 900 to 4000.

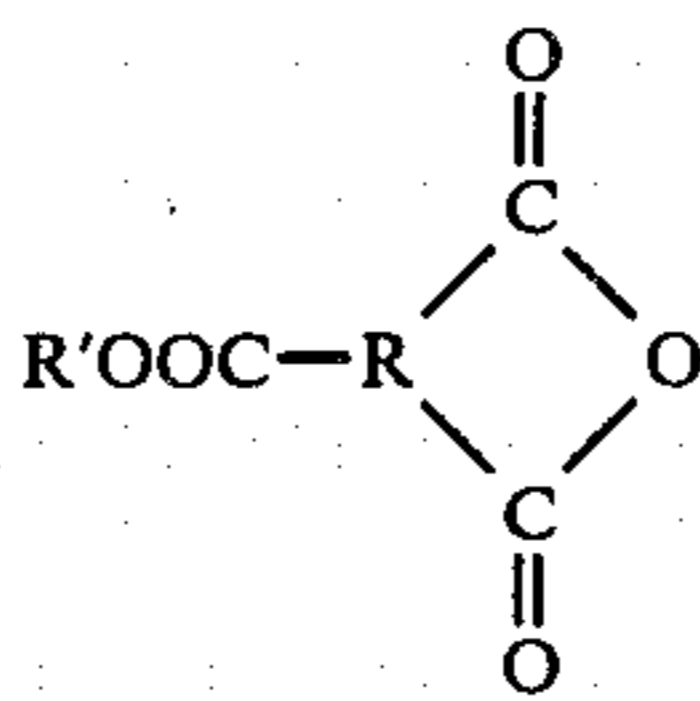
12. The composition of claim 1 wherein the polyoxyalkylene diimide diacid is derived from trimellitic anhydride and a polyoxyalkylene diamine selected from the group consisting of polypropylene oxide diamine and a copoly(ethylene oxide-propylene oxide)diamine having predominately polyethylene oxide in the backbone.

13. The composition of claim 1 wherein the weight ratio of polyoxyalkylene diimide diacid (c) to dicarboxylic acid (b) is from about 0.25 to about 2.

14. The composition of claim 1 wherein the weight ratio of polyoxyalkylene diimide diacid (c) to dicarboxylic acid (b) is from about 0.4 to about 1.4.

15. The composition of claim 1 wherein up to a minor amount of a tricarboxylic component selected from the group consisting of carboxylic acid anhydrides having an additional carboxyl group and tricarboxylic acid compounds having two vicinal carboxyl groups.

16. The composition of claim 15 wherein the tricarboxylic component is characterized by the following formula:



where R is selected from the group consisting of C₂ to C₂₀ aliphatic and cycloaliphatic trivalent organic radicals and C₆ to C₂₀ aromatic trivalent organic radicals and R' is selected from the group consisting of hydrogen, C₁ to C₆ aliphatic and cycloaliphatic monovalent organic radicals and C₆ to C₁₀ aromatic monovalent organic radicals.

17. The composition of claim 15 wherein the tricarboxylic component is trimellitic anhydride.

18. The composition of claim 15 wherein the tricarboxylic component is present in an amount up to 20 mole percent based on the moles of polyoxyalkylene diimide diacid.

19. The composition of claim 15 wherein the tricarboxylic compound is present in an amount up to 10 mole percent based on the moles of polyoxyalkylene diimide diacid.

20. The composition of claim 1 which further contains a stabilizer.

21. The composition of claim 20 wherein the stabilizer is 3,5-di-tert-butyl-4-hydroxy hydrocinnamic triester with 1,3,5-tris-(2-hydroxy ethyl)-3-triazine-2,4,6-(1H,3H,5H)trione.

22. The composition of claim 15 which further contain a stabilizer 3,5-di-tert-butyl-4-hydroxy hydrocinnamic triester with 1,3,5-tris-(2-hydroxy ethyl)-3-triazine-2,4,6-(1H,3H,5H)trione.

23. A polyetherimide ester composition comprising the reaction product of (a) 1,4-butanediol (b) dimethylterephthalate and (c) a polyoxyalkylene diimide diacid derived from trimellitic anhydride and a polyoxyalkylene diamine having the formula:



wherein G is the divalent radical remaining after removal of the hydroxy groups of a long chain ether glycol having a molecular weight of from about 600 to about 12000.

24. The composition of claim 23 wherein the long chain ether glycol has a molecular weight of from about 900 to about 4000.

25. The composition of claim 23 wherein the long chain ether glycol is selected from the group consisting of polypropylene ether glycol and co(polyethylene ether - propylene ether)glycol having a predominately polyethylene ether backbone.

26. The composition of claim 23 in which trimellitic anhydride is added as an additional reactant.

27. The composition of claim 23 which contains a stabilizer 3,5-di-tert-butyl-4-hydroxy hydrocinnamic triester with 1,3,5-tris-(2-hydroxyethyl)-3-triazine-2,4,6-(1H,3H,5H)trione.

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